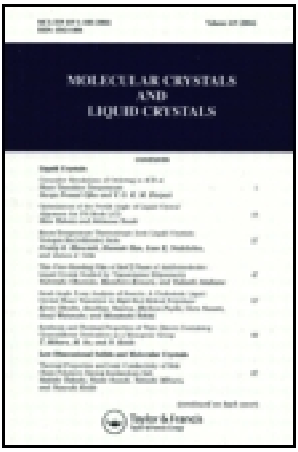

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

DSC and Optical Texture Studies of Copolymers Based on Poly(butyleneterephthalate)/PHBA and PET/PHBA

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To cite this article: K. Goranov , S. Fakirov , H. P. Hinov & A. Zheliaskova (1989): DSC and Optical Texture Studies of Copolymers Based on Poly(butyleneterephthalate)/PHBA and PET/PHBA, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 173:1, 31-48

To link to this article: http://dx.doi.org/10.1080/00268948908033365

Mol. Cryst. Liq. Cryst., 1989, Vol. 173, pp. 31–48
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Printed in the United States of America

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(*Received August 11, 1988; in final form January 27, 1989*)

Copolyesters based on poly(butyleneterephthalate) (PBT) and *p*-hydroxybenzoic acid (PHBA) were obtained by transesterification in the melt and the resulting products were characterized as to their liquid crystalline properties. Thermal transitions and the mesophases formed during heating and cooling were examined by differential scanning calorimetry and hot stage polarizing microscopy. All the polymer melts were strongly birefringent and showed nematic threaded optical textures, accompanied by randomly-distributed regions of isotropic PBT and small crystallites of PHBA oligomers. During the microscopic studies of the PET/60PHBA copolymer, regions were observed where a second nematic phase appeared if the temperature was held above 260°C for a long enough time. This can be explained by the high content of PHBA and relatively low molecular weight of the copolymer.

INTRODUCTION

In 1975 de Gennes[1] predicted theoretically that linear polymers with rigid blocks interconnected by flexible spacers in the main chain would be nematic. In the same year, Roviello and Sirigu[2] reported the observation of liquid crystal polymers with mesogenic units incorporated in the flexible main chains. Liquid crystal polyesters were discovered by Jackson and Kuhfuss[3] in 1976. These authors have reported that thermotropic liquid crystalline behaviour is obtained in copolymers based on poly(ethyleneterephthalate) (PET) and *p*-hydroxybenzoic acid (PHBA). In these copolymers, PET moieties have a flexible chain conformation while PHBA moieties have a stiff rod like conformation. Alternation of these moieties or blocks of moieties causes the formation and development of the mesophase. The initial study of Jackson and Kuhfuss has been followed by the publication of many papers[4–26] devoted to the synthesis and investigation of the physicochemical properties of the various phases existing in these copolymers. In these works the nematic texture has been observed in polyesters containing several methylene groups in the flexible spacers[3–5,9–14,19,20] while smectic phases have been observed when the spacers consist of more than ten carbon atoms in the aliphatic chain.[17,18] Viney and Windle[15] have compared the optical texture exhibited by the copolymer of 40 mole % PET and 60 mole % PHBA at different temperatures with the textures previously reported for low molecular weight liquid crystals. They have identified a smectic C at lower temperatures and a nematic one at higher temperatures. The observation of a nematic phase in such copolymers has been reported by other authors whereas the identification of a smectic C phase is rather surprising and questionable. So far, the spontaneous development of smectic textures has not been confirmed in such polymer systems. According to the experimental results of Noel *et al.*[23] the interpretation of Viney and Windle would be correct in the case of observation of disclinations with a strength of (±1) typical only for the smectic C phase.[27] However, the experimental findings of Viney and Windle[15] are not sufficient for the indentification of the observed phase as a smectic C. The occurrence of (±1/2) disclinations is rare and their absence does not represent a reliable proof for the existence of a smectic C phase. The solid-to-nematic and the nematic-to-isotropic phase transitions investigated in the above cited papers have been reversible in all cases. The existence of the nematic phase has been clearly observed. As demonstrated, the temperature ranges over which the mesophase formation occurs are generally broader in the case of polymers containing an odd number of the methylene spacer units when compared to those with an even number of units.[14,17]

The apparent need of low melting mesomorphic polymers for practical applications stimulated our efforts to synthesize a series of copolyesters by transesterification of poly(buthyleneterephthalate) (PBT) with different amounts of *p*-acetoxybenzoic acid (PABA).[28] In the present paper, some preliminary findings obtained by differential scanning calorimetry (DSC) and hot stage polarizing microscopy are reported. For the sake of comparison, the same measurements were carried out with the already studied PET/PHBA copolyesters.

II. MATERIALS AND PREPARATION OF COPOLYMERS

Commercial PBT (kindly supplied by Du Pont Co.) with an intrinsic viscosity of 0.67 (in a phenol/tetrachloroethane (PhOH/TCE) mixture, 60/40% by weight) was used. *p*-Acetoxybenzoic acid was prepared by conventional acetylation of *p*-hydroxybenzoic acid with acetic anhydride using sulphuric acid as a catalyst. The copolymers were synthesized according to the method proposed by Jackson and Kuhfuss[3] described in more details elsewhere.[28]

A mixture of PABA and PBT powders was placed in a bath preheated at 275°C and stirred at this temperature under a slow argon flow for half an hour. After a low viscosity melt was obtained, vacuum was applied and stirring was continued for about 4 hours.

The resulting products were opaque, light tan in colour and showed poor adherence to glass. During the polycondensation step, the compositions prepared with up to 30 mol % PABA remained in the molten state until the completion of the reaction. The compositions with higher molar percentages of PABA (40–80) solidified within 10 to 15 min after the start of polycondensation which hampered the further proceeding of the reaction. The contents of the reactor was dissolved in a PhOH/TCE mixture at a ratio of about 1:10 at 80°C. After cooling down to room temperature, the resulting solutions were filtered. The soluble fraction was isolated by precipitation in ethanol cooled to − 10°C while the insoluble residue was suspended in ethanol. For the complete removal of the residual PhOH/TCE mixture Sohxlet extraction with ethanol was performed for several hours. The products extracted were finely ground and vacuum dried at 80°C. The yields of the soluble fraction are given in Table I.

III. METHODS

Thermal characterization: DSC studies were carried out on a Mettler Thermal Analyzer TA 3000 in the range from 25°C to 300°C at a heating rate of 20°C per minute with samples of 10 mg in nitrogen atmosphere.

Optical microscopy: Only the soluble fractions were studied by means of a Leitz Ortholux polarizing microscope supplied with a Linkam hot stage and a controller device. The PET/PHBA copolymers were studied by means of a PZO polarizing microscope supplied with the same facilities. Small pieces of the samples were preheated between glass microscope slides at a temperature above their T_m and pressed to obtain thin films, 6–10 microns thick.

IV. RESULTS AND DISCUSSION

After transesterification of PBT with PABA the following block structure of the polymer chain is formed:

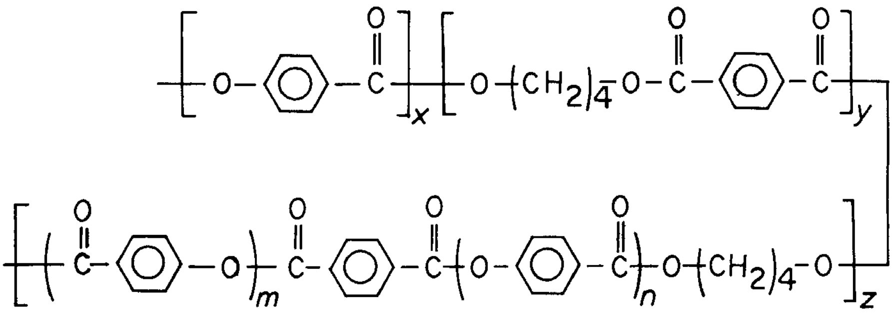


TABLE I

Thermal characteristics from DSC of the total products and the soluble fractions of PBT/PHBA copolyesters[a]

		Total product								Soluble fraction				
	Starting composition	First heating				Cooling		Second heating			First heating			
No.	mole %	T'_g	T''_g	T'_m	T''_m	T''_c	T'_c	T'_m	T''_m	wt. %[b]	T'_g	T''_g	T'_m	T''_m
1	PBT/0 PHBA	58	—	228	—	—	203	227	—	100	—	—	229	—
2	PBT/10PHBA	62	—	218	263	—	199	221	—	98	60	116	220	—
3	PBT/20PHBA	59	—	218	260	235	197	220	260	91	60	110	220	260
4	PBT/30PHBA	55	110	214	256	245	192	215	270	92	60	110	216	256
5	PBT/40PHBA	56	140	219	275	250	197	221	280	66	64	130	214	275
6	PBT/60PHBA	55	100	209	270	—	—	—	—	57	60	110	216	—
7	PBT/80PHBA	52	140	210	270	—	—	—	—	52	68	110	218	290

[a] Transition temperatures are given in °C

[b] wt. % from the total product

in which n, m and x vary from 0 to 3 and $m + n = 3$. In case $x > 3$ and $n + m > 3$ the blocks are believed to be capable to associate into infusible, insoluble crystalline domains.[16] All synthesized products contain an unmelted portion and its quantity steadily increases with the rise of PABA in the starting mixture. The solid residue does not represent a PHB homopolymer, as reported previously,[29] but it contains also a copolyester enriched in oxybenzoate moieties[7,16,25] Since these fractions are infusible, they are not examined in the present work. Only the soluble fractions of the products obtained were investigated by hot stage polarizing microscopy and DSC. All samples studied are designated by the mole percentage of PABA in the starting mixture, e.g. PBT/30 PHBA means that the sample was prepared from a mixture of 70 mole % PBT and 30 mole % PABA.

There is a lot of evidence in the literature[8,15,16,25,30] that the differences in the structure and characteristics of such copolyesters are due to irregular distribution and length of both terephthalate and oxybenzoate moieties. The different length of oxybenzoate moieties of the PBT/PHBA copolymer, under study was established using DSC, WAXS and ^{13}C NMR.[28]

III. A. THERMAL BEHAVIOUR

Figure 1 shows a set of DSC curves typical of the PBT/30PHBA total reaction product obtained consecutive heating-cooling-heating run. Upon first heating (Figure 1a) two glass transitions (T'_g and T''_g) and two melting transitions (T'_m and T''_m) are observed. Their values are given in Table I as dependent of the starting composition. The first glass transition temperature T'_g at 55°C is associated with PBT moieties in the copolymer chains. One can see from Table I that the increase of the PABA percentage in the starting mixture does not affect the T'_g value. This clearly suggests a blocky structure of the chains. Otherwise, one would expect an increase in the T'_g of PBT due to random distribution of the rigid moieties along the backbone. A similar relationship between T'_g and the type of PHBA distribution has been reported for the PET/60PHBA copolyester.[7,8,16,25,30] The higher exothermic peak T'_c (Figure 1b) could be associated with crystallization of PBT moieties and serves also as a proof of the blocky structure. The area of the T'_c exothermic peak and its position are independent on the PABA amount in the initial reaction mixture (Table I). An additional proof of the blocky nature is the existence of a second glass transition T''_g at 110°C, which could be assigned again to the amorphous regions but enriched in PHBA moieties in the copolyesther chains (Figure 1a). Both glass transitions (T'_g and T''_g) are clearly observed at almost the same temperatures for the soluble fractions (Table I). Upon cooling and second heating too (Figure 1b and 1c) there are no more indications for the existence of any glass transition (T'_g or T''_g, Figure 1a). It is suggested that under the conditions of DSC analysis a new structure of the copolymers could form after heating of the melt at temperatures above 260°C–270°C.

Upon first and upon second heating (Figure 1a and 1c) very well expressed melting peaks of PBT appear at T'_m 214°C and 216°C respectively. These melting temperatures are lower than T'_m of the PBT homopolymer (Table I), due to the incorporation of PHBA moieties in the PBT chains. Upon both heating runs (Figure

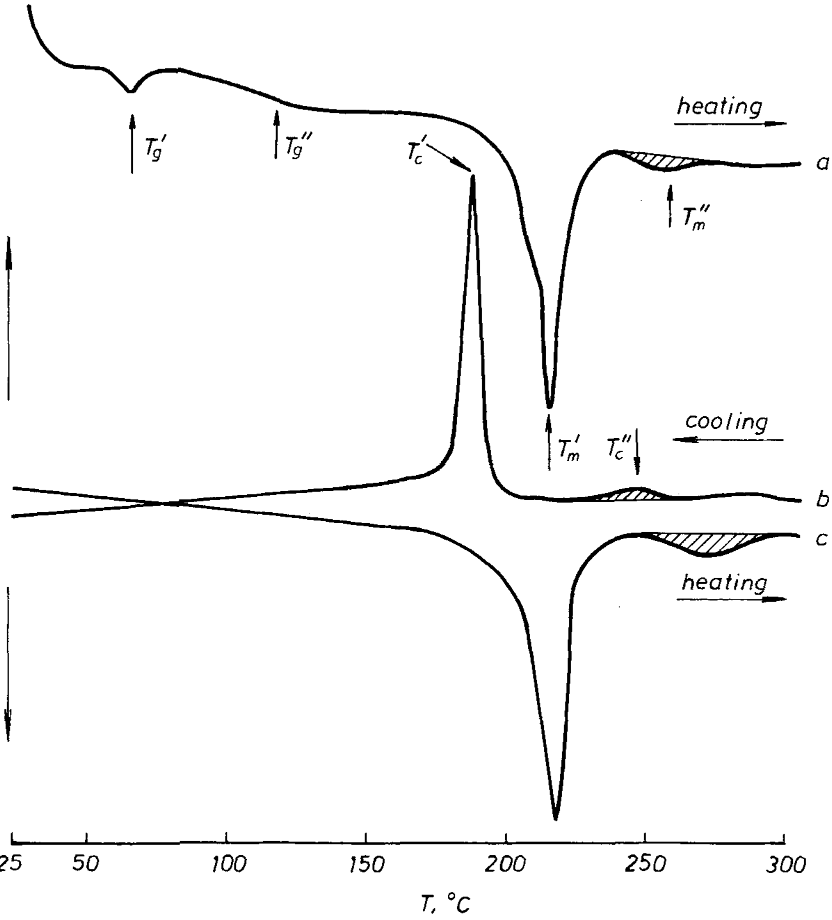


FIGURE 1 DSC curves of PBT/30PHBA (a) first heating (b) cooling (c) second heating

1a and 1c) a second relatively broad endothermic transition T''_m at 256°C can be observed (Table I). While the area and the peak position of T'_m on first heating (Figure 1a) are almost identical to those on second heating (Figure 1c), this is not the case with T''_m. After cooling (Figure 1c) T''_m appears at a higher temperature. The broad endothermic peak T''_m in both heatings could be associated to the melting of a copolyester rich in PHBA moieties and its area is about two times larger than that of Figure 1a. Similar endothermic peaks situated above the melting temperature of PET were also observed with PET/PHBA copolyesters.[12,22,24,25] An additional proof of this suggestion is the observation of crystalization upon cooling $T''_c = 245$°C (Figure 1b). The values of T''_c increase with the rise of the PABA percentage in the starting mixture (Table I).

These thermal transitions clearly show simultaneous existence of two fractions in the PBT/PHBA copolyesters which differ substantially in the PHBA content of the copolymer chains.

III. B. OPTICAL OBSERVATIONS

Since the PET/PHBA copolymers have been extensively studied, the comparison of the optical textures of the PET and PBT copolymers was very helpful in the present case. The general problems which are typical for such a study are discussed briefly. According to Mackley *et al.*,[11] the detailed birefringent textures usually observed between crossed or parallel polaroids are often complex and depend on such variables as the sample preparation including the treatment of the glass plates which confine the copolymers under study, thermal and mechanical prehistory, etc. The textures of the copolymers were observed in both the true liquid crystalline state at high temperatures and the frozen-in liquid crystalline state at low temperatures. In order to observe transmitted light through the material, the samples should be much thinner than the conventional samples prepared from low molecular weight liquid crystals.[11] Our samples were 6 to 10 microns thick, which was sufficient to observe birefringent textures typical of thermotropic liquid crystals. Despite the presence of air bubbles observed, it was clear that the polymer samples under study had an almost constant thickness since simultaneous existence of thick and thin regions[11] was not observed.

a) Optical observations of soluble copolymers based on PBT/PHBA

The optical texture of the PBT/10PHBA copolymer near the solid-liquid phase transition (T = 212°C) is shown in Figure 2. An increase of the amount of PABA in the starting mixture (sample PBT/20PHBA) leads to a considerable change of the optical texture above the solid-liquid crystalline phase transition (Figure 3a, T = 265°C) and the isotropic phase (Figure 3b, T = 350°C). The texture of Figure 3a clearly shows the coexistence of the isotropic phase of the non-reacted part of PBT (the bright regions in the picture), the crystalline phase of the oligo PHBA (OPHBA) evident from the very small crystallites dispersed throughout the isotropic polymer and the birefringent thread parts of the nematic liquid crystalline polymer. In Figure 3b, one can see only the larger crystals of OPHBA embedded in the isotropic liquid phase of the unreacted polymer and the isotropic phase of the nematic copolymer. The increase of the amount of PABA above 30 mole % in the starting mixture leads to the observation of more typical liquid crystalline textures as shown in Figure 4a (PBT/40PHBA, T = 305°C), Figure 4b (PBT/60PHBA, T = 220°C), Figure 4c (PBT/60PHBA, T = 325°C) and the frozen-in liquid crystalline textures shown in Figure 5a (PBT/80PHBA, T = 210°C) and Figure 5b (PBT/80PHBA, T = 195°C). All these textures clearly demonstrate the coexistence of either isotropic PBT, liquid crystalline nematic thread textures and small crystallites of OPHBA (Figures 4a, 4b, 4c) or the coexistence of crystalline PBT, frozen-in liquid crystalline nematic phase and dispersed small crystallites of OPHBA (Figure 5b). Raising the temperature up to 370°C leads to the clear phase separation of the isotropic phase of the liquid crystalline state, isotropic PBT, and the crystal of OPHBA evident from the large number of small crystallites dispersed in the two fluids, as shown in Figures 6a (PBT/40PHBA) and 6b (PBT/60PHBA). From these pictures it is clear that there is a distinct phase separation of the two isotropic phases characterized by their different viscosities observed under the

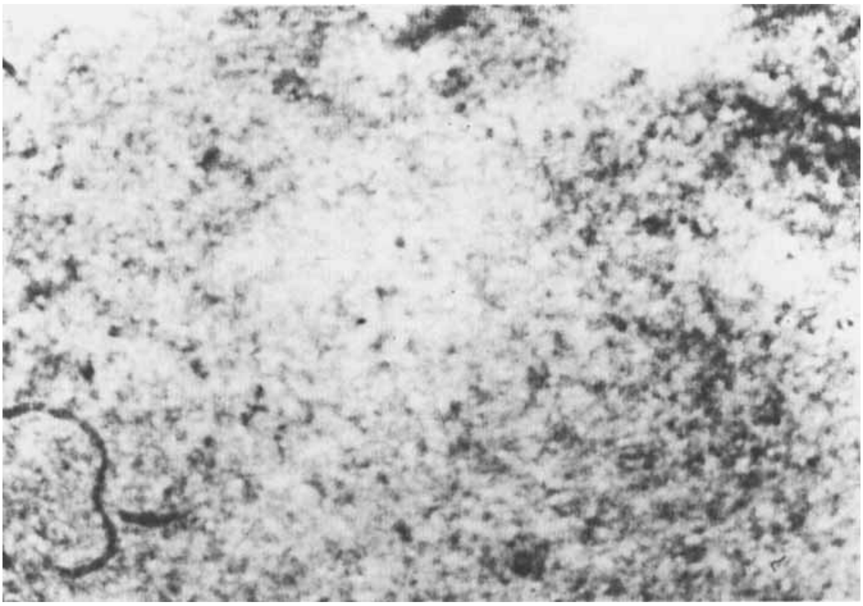


FIGURE 2 PBT/10PHBA copolymer around the solid-liquid phase transition, $T = 212°\mathrm{C}$, P 45° A, d 10 microns, magnification × 120

microscope and revealed by the thick dark lines clearly seen in Figure 6. In addition, the extensive hydrodynamics of the two fluids at this high temperature leads to the non-random distribution of OPHBA crystallites concentrated chiefly around the thick dark lines. As far as the liquid crystalline textures are concerned, (shown in Figures 3 to 5) they are typical of thermotropic nematic polymers and are observed and discussed by a number of authors.[10-15,20,21,23-26] The only difference which we should note is the superimposing of the isotropic nonreacted part of PBT and the crystalline OPHBA.

b) Optical observations of copolymers based on PET/PHBA

The preparation of PET/60PHBA samples for optical studies is identical to that of the copolymer samples based on PBT/PHBA. Many samples have been studied under the polarizing microscope. We shall discuss however only some typical features revealed after repetition of the heating-cooling cycles followed by holding the temperature at different stages. The textural observations are shown in Figures 7a to 7e as follows:

b1) The microphotographs shown in Figures 7a to 7b were taken after holding the temperature at 265°C (a nematic state) for 15 minutes and 20 minutes, respectively.

b2) Figure 7c shows a nematic texture after holding the temperature at 265°C for 30 minutes, raising up to 290°C and lowering to 202°C. Consequently this picture shows a frozen-in nematic polymer.

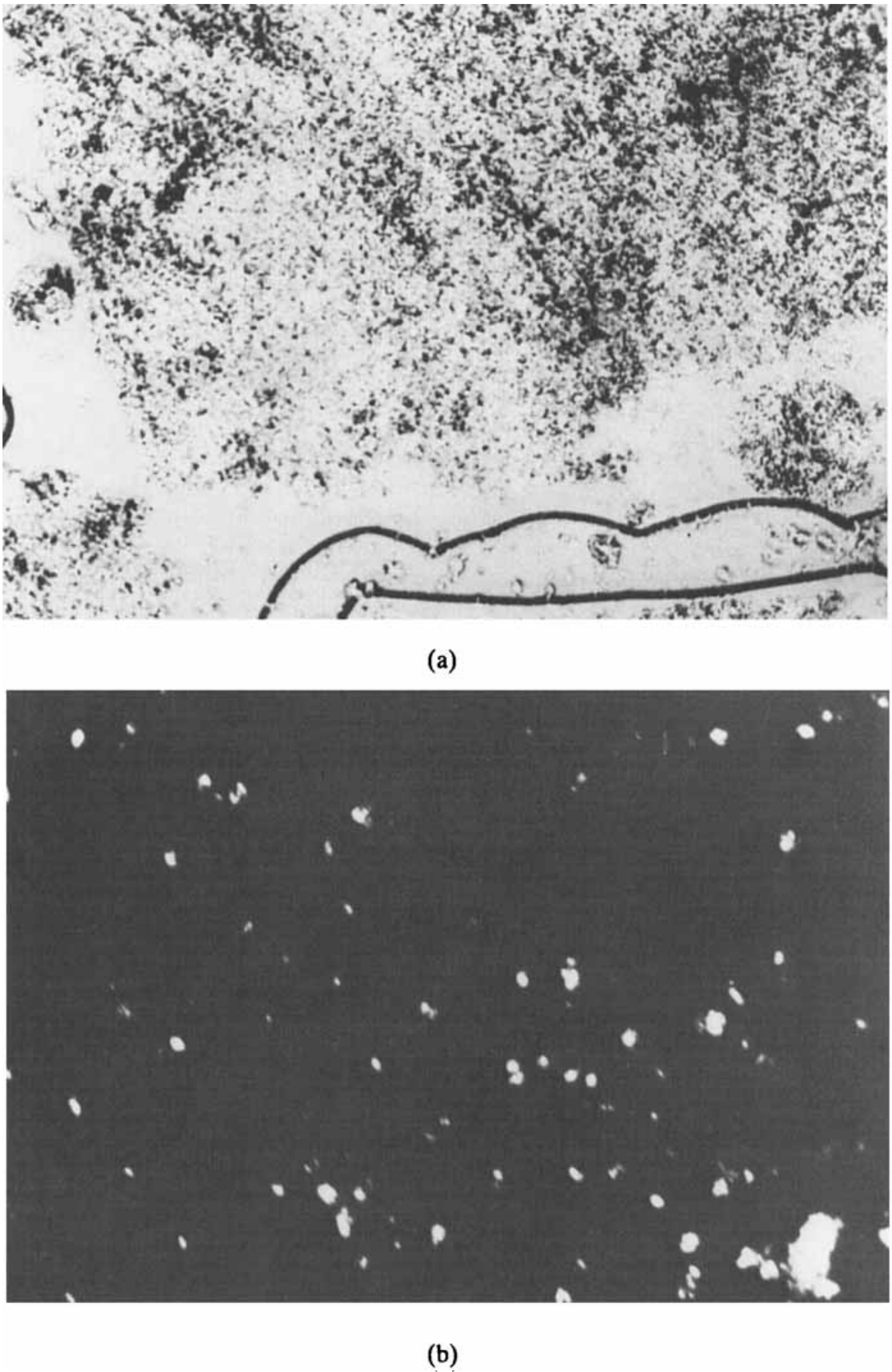


FIGURE 3 PBT/20PHBA copolymer in liquid-crystalline and isotropic phases, P 45° A, magnification × 120 (a) $T = 265°C$, obtained at the heating of the sample from $T = 212°C$ (the melting temperature) (b) $T = 350°C$, obtained after heating of the sample from $T = 265°C$

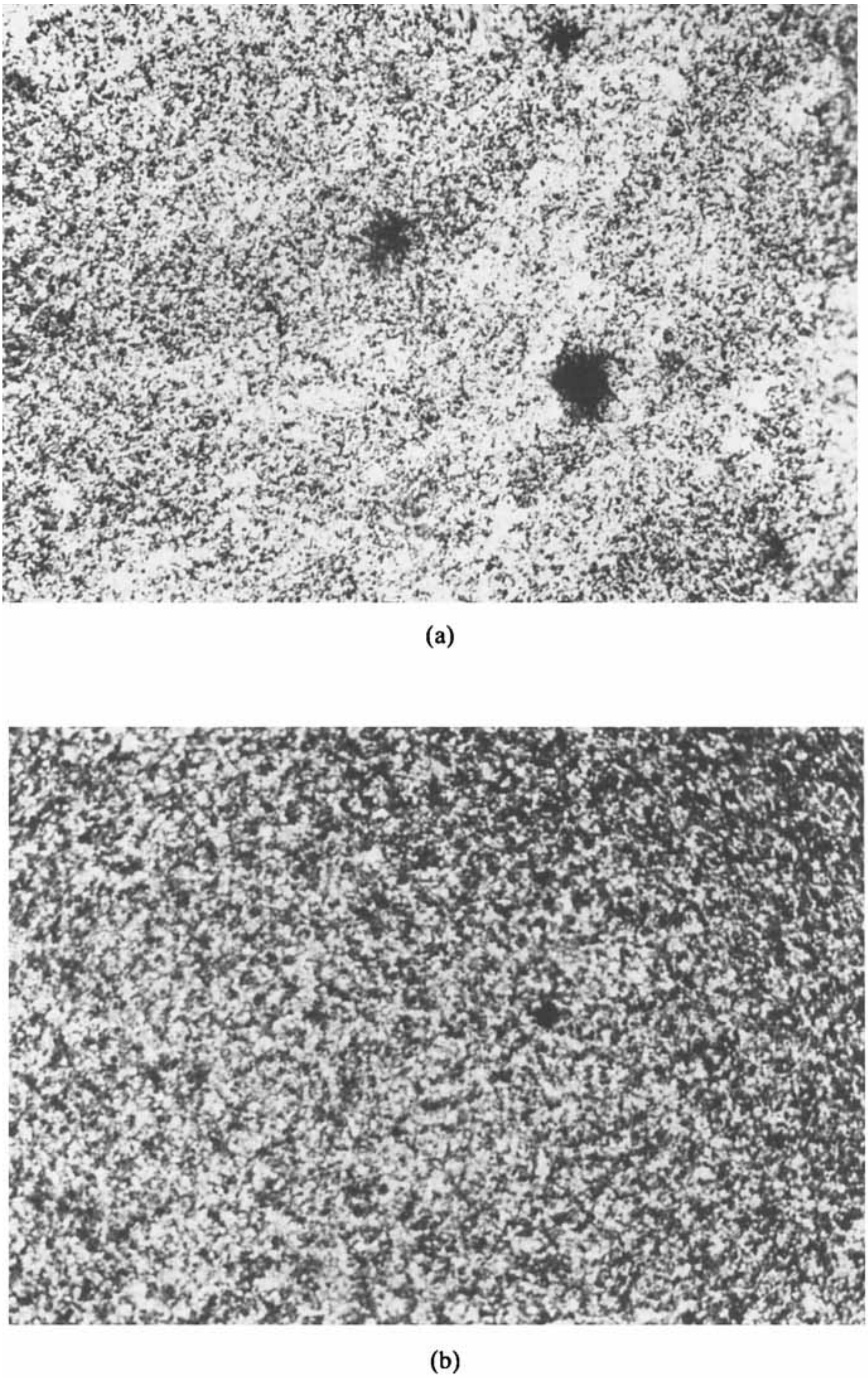
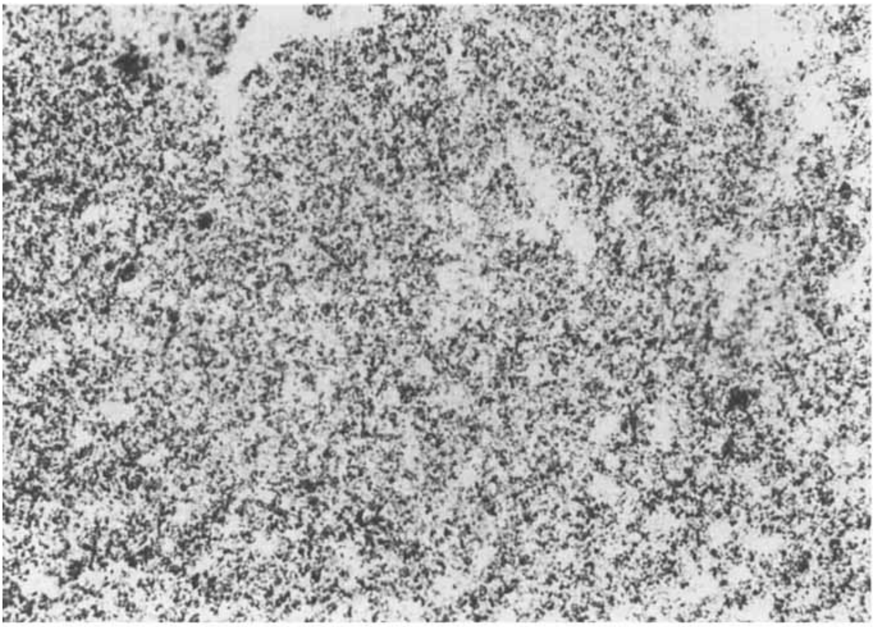


FIGURE 4 PBT/PHBA copolymers in the liquid crystalline state, P 45° A, magnification × 120 (a) PBT/40PHBA, T = 305°C (b) PBT/60PHBA, T = 220°C (c) PBT/80PHBA, T = 325°C

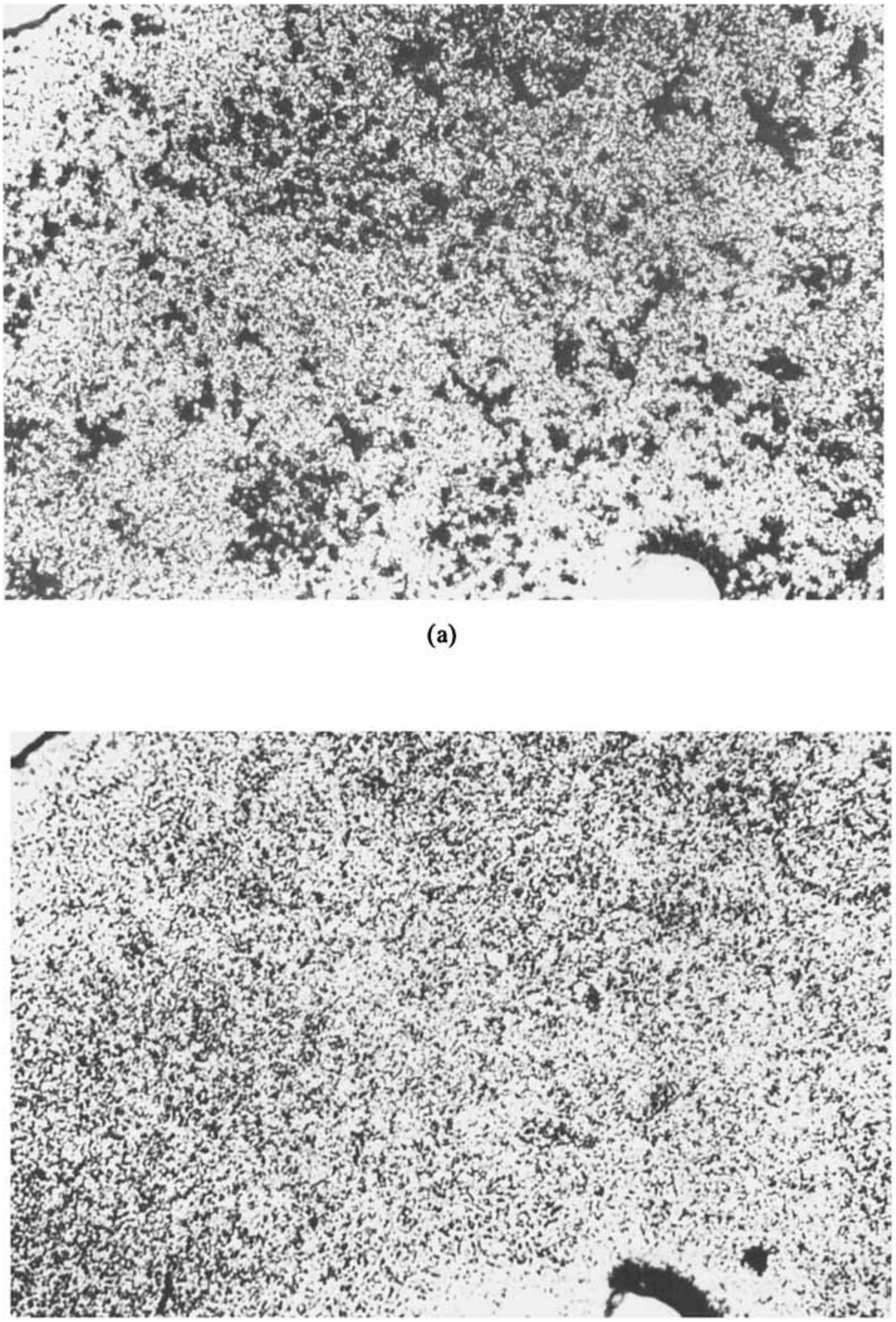


(c)

FIGURE 4 *continued*

b3) Figures 7d and 7e show a typical nematic texture after decreasing of the temperature from 290°C to 270°C and from 340°C to 230°C, respectively.

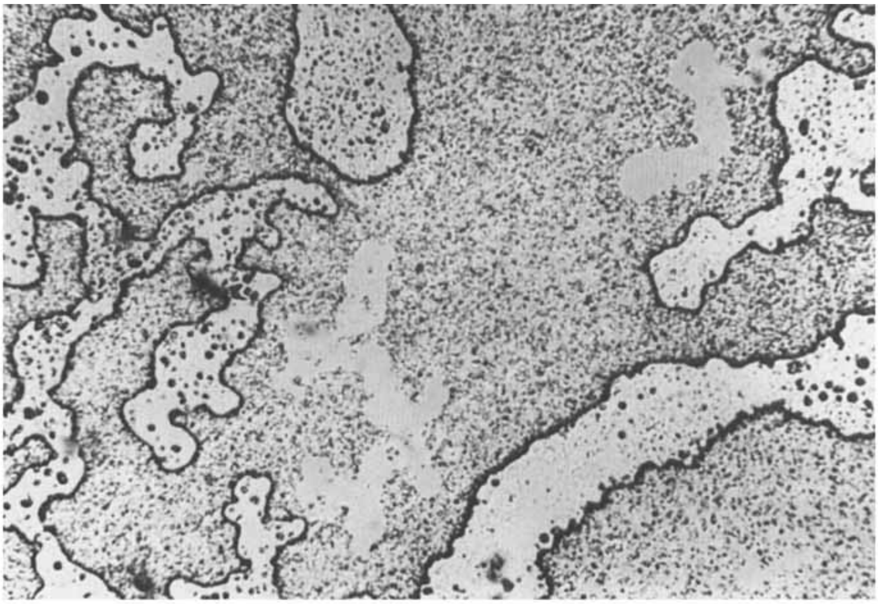
It is necessary to focus our attention on the two rings visible in Figure 7a being in the corner of the photo. With time, the size of these rings gradually increases and they could freely move within the nematic phase (see Figures 7a and 7b). Raising the temperature considerably orients the director inside these regions. The microscopic observations clearly show that the director is oriented almost homeotropically. The regions with a homeotropic orientation of the nematic phase between crossed polaroids are dark. By pressing on the cover glass plate the sample becomes brighter for a short time since the orientation is disturbed. Consequently such regions are birefringent. To distinguish between homeotropic and other tilted (or planar) orientations of the nematic phase one simply rotates the sample in a plane perpendicular to the direction of light propagation. In the case of uniform homeotropic orientation when the director is perpendicular to the glass plates, there is no change in the transmitted light, i.e. the field of view is dark between crossed polaroids. In the case of uniform tilt of the director, with the rotation of the sample the field of view gradually becomes brighter. For instance, the dark regions visible in Figure 7d demonstrate a homeotropic orientation of the director, since with the rotation of the sample the dark field of view does not change. The homeotropic or tilted orientation of the nematic director between crossed polaroids can be designated under conoscopic observations as well. For instance, the conoscopic figure of uniaxial homeotropic is a Maltese cross with a closed center. This



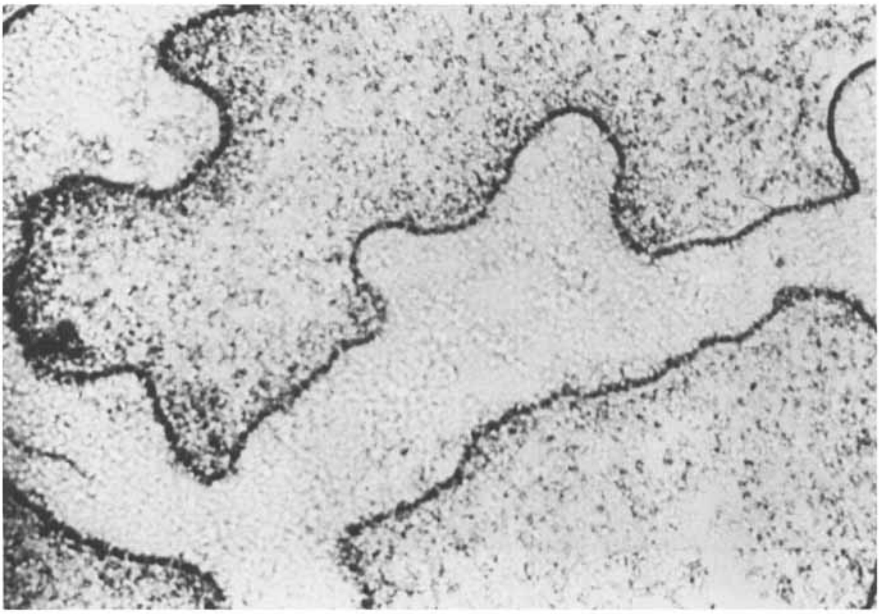
(a)

(b)

FIGURE 5 PBT/PHBA copolymer in the frozen-in liquid crystalline state, P 45° A, magnification × 120 (a) PBT/80PHBA, T = 210°C (b) PBT/80PHBA, T = 195°C

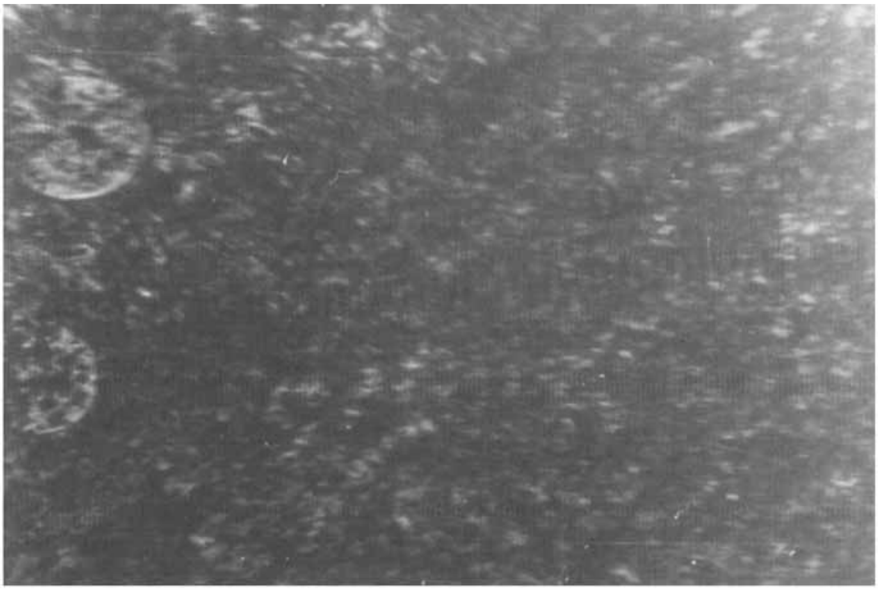


(a)

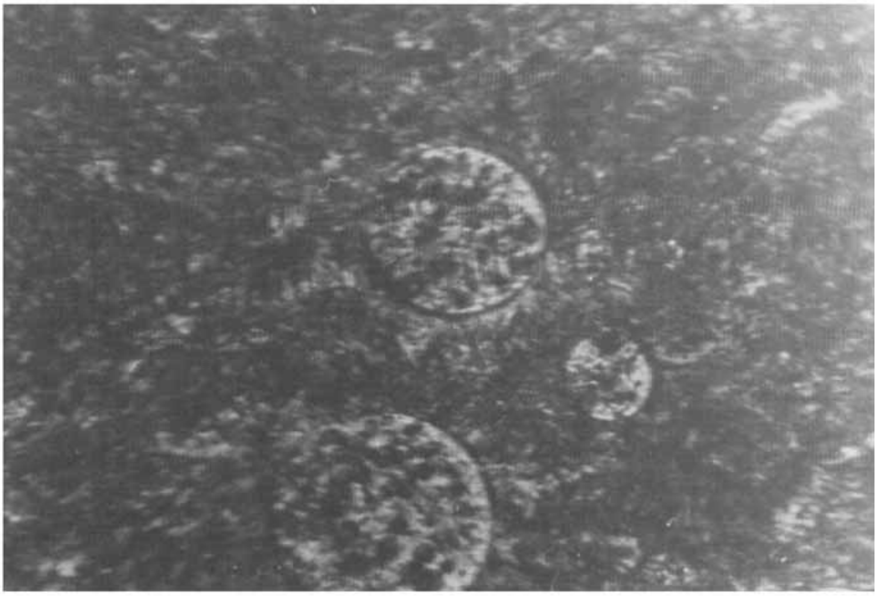


(b)

FIGURE 6 PBT/PHBA copolymers in the isotropic phase, P 45° A, magnification × 120 (a) PBT/40PHBA, T = 370°C (b) PBT/60PHBA, T = 370°C

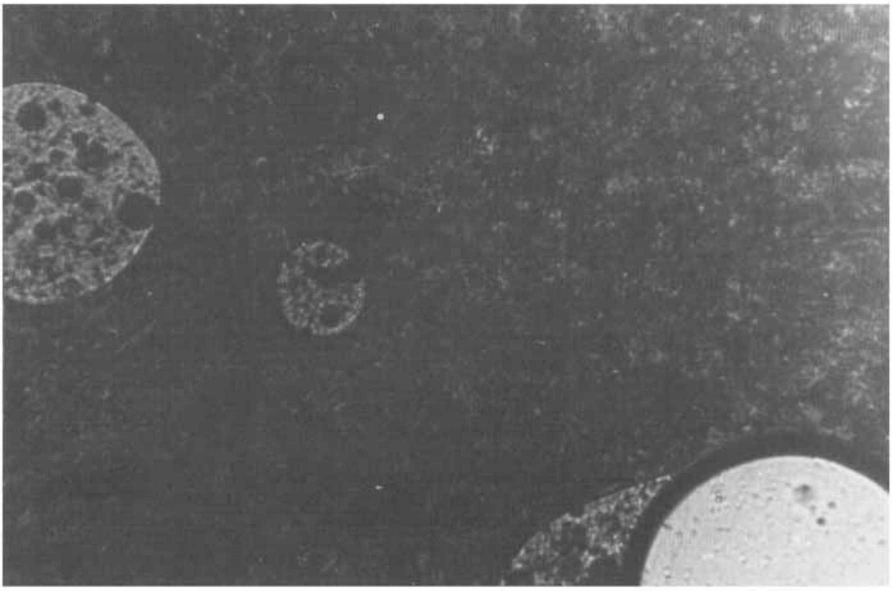


(a)

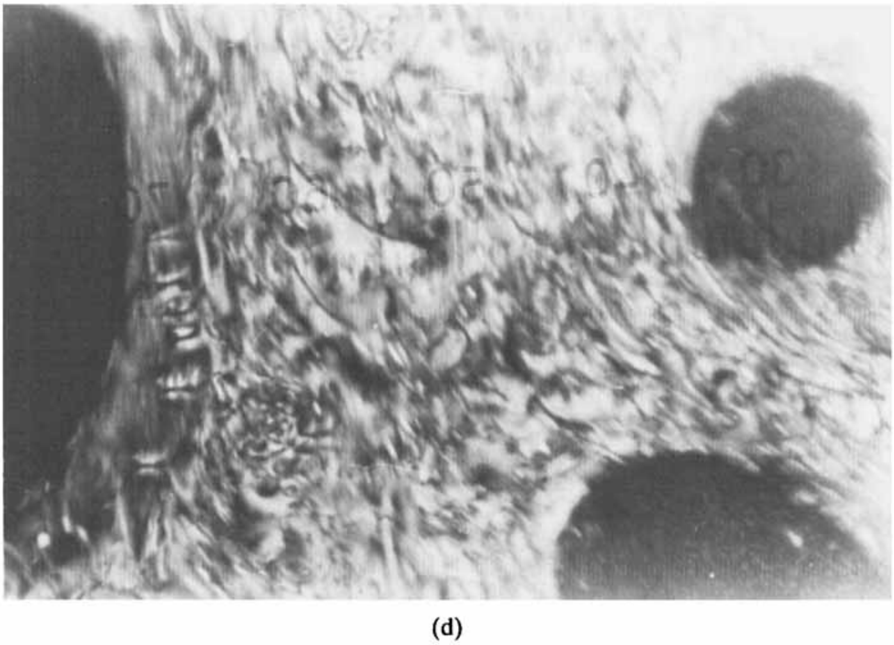


(b)

FIGURE 7 Different phases of PET/60PHB copolymer: (a)–(c)—P // A (d)–(e)—P I A, 10 small divisions correspond to 83 microns (a) nematic phase and rings at T = 265°C after holding temperature for 15 minutes (b) nematic phase and rings at T = 265°C after holding the temperature for 20 minutes (c) frozen-in nematic phase and rings at 202°C (d) nematic phase and rings at the second cooling T = 270°C (e) nematic phase and rings at the second cooling T = 230°C

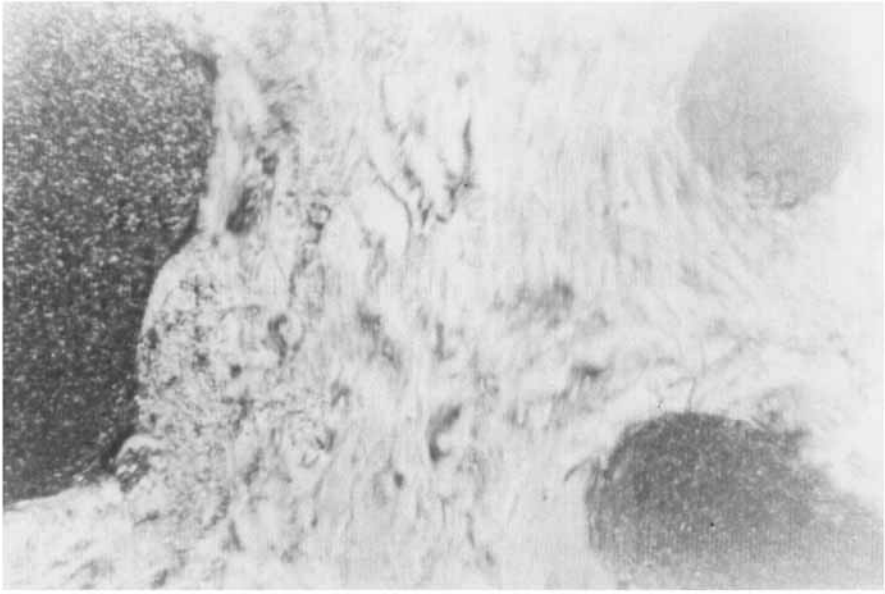


(c)



(d)

FIGURE 7 *continued*



(e)

FIGURE 7 *continued*

cross does not change with the rotation of the sample. However it changes with orbitrary rotation of the two polaroids. On the other hand the conoscopic figures of a tilted uniaxial orientation are very complex. In this study we have investigated the textures under the polarizing microscope in a transmitted white light. The use of conoscopic technique in our study was impossible.

Let us now stress that such rings have been already observed by Mackley, Pinaud and Siekmann,[11] by Joseph, Wilkes and Baird[25] and discussed by Lenz and Windel.[31] It seems also that similar however non-circular regions have been observed and by Meurisse *et al.*[22] in the polyester T029. The explanation given by these authors is very interesting and important. According to Mackley *et al.*[11] emergence of the ring domains at elevated temperatures is associated with some form of chemical or physical segregation process due to differences in chemical composition or molecular weight. According to Joseph *et al.*[25] the difference in texture in the light and dark areas is caused by a difference in anisotropy, possibly due to differences in the relative amounts of PHBA present in each phase. Joseph *et al.* concluded that molecular rearrangement begins to occur at temperatures in the range of 220°C–230°C. They speculated that differences in depolarization that occur due to anisotropy difference are associated with the presence or absence of oriented PHBA rich regions. They showed that upon heating the material to higher temperatures, for example 275°C–285°C, further structural rearrangement occurs with domains in the 12 micron range with textures similar to nematic-like liquid crystalline system being formed. According to Meurisse *et al.*[22] and Lenz[31] there is a coexistence of nematic and isotropic regions over a wide temperature interval.

Taking into account the optical observations shown in Figures 7a to 7e, together with the assumptions of the above cited authors and the DSC results comment in the preceeding part of this paper, we can conclude that the circular and non-circular regions being formed at elevated temperatures higher than 260°C after holding of temperature for up to 30 minutes are regions rich in PHBA. At higher temperatures they represent a lower molecular weight nematic phase when compared to the other PET/PHBA regions. They also have a strong tendency to orient themselves homeotropically. Consequently there is a coexistence of two immiscible nematic phases which are different in molecular weight of PHBA content. Let us also mention that Ringsdorf, Schmidt and Schneller[32] have obtained very similar ring domains in mixtures of polymeric and low molecular weight liquid crystals. By decreasing the temperature in our case, the homeotropic orientation of the lower molecular weight liquid crystal loses the orientation which is evident from Figures 7c and 7e. However, the frozen-in liquid crystalline phase that appears in the dark regions visible in Figure 7e at $T = 230°C$ can be either nematic or smectic. Further studies accompanied by the application, for instance of an electric field is needed to clarify this point.

The second important conclusion which can be made from these observations is that during the second heating run of the sample, at a relatively low temperatures, one can obtain a very clear nematic texture shown in Figure 7d. One can see in this photograph separate nematic treads.

Finally, let us note that very similar results were obtained from the copolymers based on PBT/PHBA. These results accompanied by investigation with electric fields will be published in the future.

IV. CONCLUSION

All the copolymers described in the present work exhibited thermotropic liquid crystalline behaviour which depends on the amount of PHBA in the polymer chain. The copolymers produced from 20 to 30 mole % PABA in the starting mixture as well as the soluble fractions for samples with higher PABA content led to turbid melts and showed strong stir opalescence. Typical nematic thread-like structures accompanied by randomly distributed regions of isotropic PBT and small crystallites of OPHBA were observed by a hot stage polarizing microscopy. The transitions from solid to nematic and from nematic to isotropic phases were reversible in all cases and became better defined, after repeated heating and cooling cycles, than the textures observed upon the first heating. After cooling a PBT/30PHBA sample previously preheated at 320°C, a new crystalline phase was created which quickly melted in the range of 350°C–360°C. Some of the texture changes established by visual observation were not noticeable in DSC scans. Although in the case of thermotropic polyesters on heating-cooling runs the endotherms T''_m and corresponding exotherms T''_c have already been associated with liquid crystal-to-isotropic and isotropic-to-liquid crystal phase transitions, respectively,[18] for the PBT/PHBA copolyesters studied there is no evidence for such transitions in the temperature range of 250°C–280°C. The liquid crystalline phase of the PBT/PHBA copolymers appears at 20 mole % of PHBA while for the PET/PHBA copolymers this mesophase forms at 30 or 40 mole % of PHBA. During the study of PET/60PHBA copolymers at appropriate temperatures above 260°C and holding for a sufficiently long time, regions of a second nematic phase were observed probably because of the richer content in PHBA and lower molecular weight of the copolymer.

References

1. P. G. de Gennes, *C. R. Acad. Sci.*, Paris, **B281**, 101 (1975).
2. A. Roviello and A. Sirigu, *J. Polym. Sci., Polym. Lett. Ed.*, **13**, 455 (1975).
3. W. J. Jackson, Jr and H. F. Kuhfuss, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 2043 (1976).
4. A. C. Griffin and S. J. Havens, *Mol. Cryst. Liq. Cryst. Lett.*, **49**, 239 (1979).
5. A. C. Griffin and S. J. Havens, *J. Polym. Sci., Polym. Lett. Ed.*, **18**, 259 (1980).
6. W. J. Jackson, Jr, *Brit. Polym. J.*, **12**, 154 (1980).
7. J. I. Jin, S. Antoun, C. Ober and R. W. Lenz, *Brit. Polym. J.*, **12**, 132 (1980).
8. J. Menczel and B. Wunderlich, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1433 (1980).
9. R. W. Lenz and J. I. Jin, *Macromolecules*, **14**, 1405 (1981).
10. S. Antoun, R. W. Lenz and J. I. Jin, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1901 (1981).
11. M. R. Mackley, F. Pinaud and G. Siekmann, *Polymer*, **22**, 437 (1981).
12. A. C. Griffin and S. J. Havens, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 951 (1981).
13. A. Zachariades, J. Economy and S. A. Loga, *J. Appl. Polym. Sci.*, **27**, 2009 (1982).
14. C. Ober, J. I. Jin and R. W. Lenz, *Polymer J.*, **14**, 9 (1982).
15. C. Viney and A. H. Windle, *J. Mat. Sci.*, **17**, 2661 (1982).
16. R. W. Lenz, J. I. Jin and K. A. Feichtinger, *Polymer*, **24**, 327 (1983).
17. A. H. Khan, J. E. McIntyre and A. H. Milburn, *Polymer*, **24**, 1611 (1983).
18. C. Ober, J. I. Jin and R. W. Lenz, *Makromol. Chem., Rapid Commun.*, **4**, 49 (1983).
19. M. Kleman, L. Liebert and L. Strzelecki, *Polymer*, **24**, 295 (1983).
20. C. Viney, G. R. Mitchell and A. H. Windle, *Polymer Commun.*, **24**, 145 (1983).
21. C. Ober, J. I. Jin and R. W. Lenz, *Adv. Polym. Sci.*, **59**, eds. M. Gordon and N. A. Plate, Springer Verlag (Berlin), 104 (1984).
22. P. Meurisse, C. Friedrich, M. Dvolaitzky, F. Laupretre, C. Noel and L. Monnerie, *Macromolecules*, **17**, 72 (1984).
23. C. Noel, C. Friedrich, F. Laupretre, J. Billard and C. Strazielle, *Polymer*, **25**, 263 (1984).
24. C. Noel, F. Laupretre, C. Friedrich, B. Fayolle and L. Bosio, *Polymer*, **25**, 808 (1984).
25. E. Joseph, G. L. Wilkes and D. G. Baird, *Polymer*, **26**, 689 (1985).
26. N. J. Alderman and M. R. Mackley, *Faraday Discuss. Chem. Soc.*, **79**, 149 (1985).
27. D. Demus and L. Richter, "Textures of Liquid Crystals", *Verlag Chemie*, Weinheim, (1974).
28. K. Goranov, S. Fakirov and H. Zachmann, to be published.
29. K. Ober, *Ph.D. Thesis*, Amherst, USA (1982).
30. J. Economy, private communication.
31. General discussion, *Far. Discuss. Chem. Soc.*, **79**, 91 (1985).
32. H. Ringsdorf, H. W. Schmidt and A. Scheller, *Makromol. Chem., Rapid Commun.*, **3**, 745 (1982).